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No. IV.

Miscellaneous Experiments relating to the Doctrine of Phlogiston. By Dr. Joseph Priestley.

IT has been faid that the fixed air which I get by heating iron in dephlogisticated air, comes from the plumbago contained in the iron, and that when it is found after the union of inflammable and dephlogisticated air, it was from plumbago dissolved in the inflammable air. But besides that there is no evidence of inflammable air containing any plumbago (since when iron is dissolved in any acid the plumbago is left behind) the fixed air contained in this substance is very inconsiderable, the bulk of the air into which it may be resolved being inflammable.

From 6 dwts. of the finest plumbago from an iron furnace, in the form of a light powder, I got in a glazed earthen tube 40 ounce measures of air, one-twelfth part only of which was fixed air, and the rest inslammable, burning with a blue slame. Then sending steam through it, I got 240 ounce measures more, the whole of which was inflammable, of the purest kind, exactly resembling that from iron by the acid of vitriol. The plumbago was concreted into one mass, resembling a hard cinder, and weighed $2\frac{1}{2}$ dwts.

Another experiment on plumbago I shall mention in this place. Melting one dwt. of it with a burning lens, it threw out sparks, like cast iron treated in the same manner, but not quite so much; after which it was reduced to a slag, like sinery cinder, weighing 4 grains less than it had done. I repeated the experiment with the same result.

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2. The experiments on the revival of precipitate per fe in inflammable air being differently reported by different experimenters, and being fometimes attended with hazard, I shall add the following, which were made feveral years ago, to those which I have made and repeated since.

In 9 ounce measures of inflammable air from malleable iron and water I revived part of the precipitate sent me by Mr. Berthollet, which I had found to contain no fixed air, till not more than one-fourth of the air remained unabsorbed; on examination, I found about one-twentieth part of it fixed air; but mixing nitrous air with it, it appeared that the air dislodged from the precipitate had not united with the inflammable air; for the standard of equal measures of them was 1.71. After the process I missed 18 grains of the precipitate. But there are several causes of loss in this case, besides the quantity of air expelled from the substance.

In 5.5 ounce measures of the same inflammable air I revived some of the same precipitate till it was reduced to 0.77 ounce measures. Of this one-sixth part was fixed air, and the residuum of the standard of 1.6. It exploded at once when the slame of a candle was presented to it.

3. As pyrophorus imbibes pure air when it is exposed to atmospherical air, leaving nothing but phlogisticated air, (in which it resembles a mixture of iron silings and sulphur, which also makes a pyrophorus,) the fixed air expelled from it afterwards must have been formed by the union of the pure air imbibed by it and the phlogiston contained in itself.

From a quantity of old and fpoiled pyrophorus I got 180 ounce measures of air, of the first part of which one half was fixed air, and the rest phlogisticated. At the last, the one half was fixed air, and the rest was inflaminflammable. In another experiment of this kind I found seven-tenths of the air fixed, and the rest inflammable.

The fixed air that is expelled from lime which has been long exposed to the atmosphere cannot have any other origin than the pure air that it has imbibed and some phlogiston which it derived from the fire; for the air to which it is exposed is always something less pure than it was before.

From 15 dwts. of fallen lime I got 45 ounce measures of fixed air, and 25 inflammable from the gun barrel in which the experiment was made. Whether quicklime has been exposed to the atmosphere, so as to become what is called fallen lime, or has been saturated with water, they come in time to be of the same weight, and to have the same properties; the former continually gaining weight, and the latter losing it.

From 15 dwts. of lime saturated with water, and then exposed to the atmosphere, I got 55 ounce measures of fixed air.

4. If any metal be calcined in common air over lime water, a very thick feum will be formed on its furface, and much of the air will be imbibed by the calx that is formed. I have recited the result of this process with several of the metals, and I shall now observe that I had the same result with platina, silver, and gold. In the experiment with platina 33 ounce measures of air were reduced to $26\frac{1}{2}$, of the standard of 1.75.

5. That phlogisticated air is sometimes formed by the union of dephlogisticated air and phlogiston is as clearly proved by experiment as that fixed air is formed from the same elements. One proof of this is that common air can never be diminished so much by the purest dephlogisticated air as it may be by nitrous air, the residuum in both the cases being alike phlogisticated air. I

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could not by any mixture of dephlogisticated and inflammable air, fired by an electric spark, reduce it to less than 2.5; whereas by nitrous air the same dephlogisticated air was diminished to 0.04; so that there must have been a production of phlogisticated air when the inflammable air was used.

If after any diminutions of common air by phlogistic processes more phlogisticated air is found in some of them than there is in others, the additional quantity must have been formed in the process; and that there is a great variety in these results I have observed before.

Heating fine needles in common air over mercury till, after its greatest diminution, it was increased to its original bulk, I found that it had nothing sensibly inflammable in it, but was wholly phlogisticated; whereas the addition of one-fourth of inflammable air to three-fourths of phlogisticated air was easily distinguishable by the slame of a candle. Fixed air will be produced in this process if it be made over lime water, but not with certainty in any other circumstances.

When substances that diminish air, and leave it phlogisticated, emit inflammable air before and after the process, it is reasonable to conclude that they did the same during the process; and since nothing inflammable is found in the air after it, that it united with the pure part of the air to which it was exposed, and by that union formed part of the phlogisticated air; so that less of this kind of air existed in the atmosphere than has generally been supposed. This I have observed to be the case with a mixture of iron filings and sulphur. It was the same with iron that had been partially dissolved in vitriolic acid. After diminishing a quantity of air I immersed it in mercury, and it gave out a small quantity of inflammable air.

I have recited one case of phlogisticated air being formed by exposing rusted iron to inflammable air, which must have been formed by the oxygen in the rust and the phlogiston in the air. There is, however, much uncertainty in this result, depending on circumstances which I have not been able to ascertain. But one clear case of the kind is sufficient proof of the hypothesis, and I have met with several.

On the 15th of August 1799 I examined a quantity of inflammable air which had been confined by mercury with dry iron rusted in nitrous acid from the 18th of March 1798, and found nothing inflammable in it, though there was no apparent change in the colour of the iron. This was also the case of another quantity of the same kind of air which had been confined in the same manner from the 14th of July. At the same time, however, another quantity of inflammable air that had been confined the same time, and in the same manner, with iron rusted in vitriolic acid was not much changed, though the iron was become black.

Since pure nitrous air wholly vanishes when it unites with pure dephlogisticated air, the phlogisticated air that is found after heating iron in it must have been formed from some oxygen contained in the nitrous air and phlogistion from the iron. After heating turnings of cast iron in $5\frac{1}{2}$ ounce measures of nitrous air from mercury it was reduced to $3\frac{1}{2}$ ounce measures, and by washing in water to $2\frac{1}{2}$, one ounce measure having been fixed air. But when I heated malleable iron in 60 ounce measures of the same nitrous air it was reduced to 24 ounce measures, all phlogisticated. When I continued this process beyond the point of greatest diminution, the air produced was inflammable.

Since water contains but a fmall quantity of air in proportion to its bulk, and generally confiderably purer than that

that of the atmosphere, the phlogisticated air that is found by heating steam in a copper vessel must have been formed from phlogiston in the copper, and the pure part of the air contained in the water; and whenever I have heated water in this manner and have kept it a considerable time in the form of steam, I have found a quantity of air completely phlogisticated, and the longer I kept it in this state the more of this air I found.

I have observed that when metals are calcined in common air over water, the air is always diminished, and if it be done over lime water, fixed air is produced. If the calcination be continued after the greatest diminution of the air, it will be increased by an addition of inflamma-If this inflammable air came from the decomposition of the water, the water over which the process was made would either be acid, or contain pure air, but this is never the case. This water is both free from all acidity, and gives out air less pure than that of the atmosphere. Also the air confined in the same phial with it is less pure than that of the atmosphere. If the oxygen of the water entered into the calx that is formed, hydrogen, or inflammable air, ought, according to the new theory, to be formed, which it is not.

Also air from water in which mercury has been agitated is considerably worse than common air. A candle went out in it. Had the black powder which is formed in this process been owing to the decomposition of the water, since this powder is mercury super-phlogisticated, the remaining water would have been in a state of oxygenation; and therefore the air exposed to it would have been purer than that of the atmosphere.

It is faid that metals become calces by imbibing oxygen; but no oxygen has yet been discovered in finery cinder, and very little, if any, in flowers of zinc. If minium or red precipitate, be dissolved in marine acid, none of the Vol. V.

dephlogisticated air which these substances contain is then extricated; but if the solutions be evaporated, and the dry residuum be heated by a burning lens, the pure air is evolved. For the common air in which they are heated receives an addition of pure air. But the reverse is the case when the solutions of sincery cinder or slowers of zinc are treated in the same manner.

I heated a folution of the purest flowers of zinc in marine acid in common air, and observed that it emitted a dense white vapour for about an hour after it was evaporated to dryness. The air was but little diminished, but worse than common air, in the proportion of 1.45 to 1.35.

I have observed that common air which has been exposed to hot charcoal is both diminished and phlogisticated, but that the air which by immersion in water comes out of this charcoal is likewise phlogisticated. This proves the generation of phlogisticated air in the process. The water over which this process is made also gives out air less pure than that of the atmosphere.

Charcoal that had been exposed in common air under a receiver some days, did not, when immersed in water, give out more than half as much air as charcoal heated and put into water immediately after it was cold. Both being placed near the fire, still immersed in water, gave out more air, but in the same proportion. Also, standing in this situation a long time made no difference in this case.

6. That finery cinder contains nothing but water and calx of iron, I think I have sufficiently proved by several observations, especially by its enabling hot charcoal to give out the same kind of air that water will do. I had a similar result with terra ponderosa aerata, which gives no fixed air with mere heat, but does it when red hot by means of water.

I mixed a quantity of this substance pounded with pounded finery cinder; and putting it into a gun barrel, got from it fixed air as copiously as if a stream of water had passed over it. There was a considerable residuum, which was inflammable air from the iron.

- 7. Dr. Woodhouse observes that if the manganeze be heated in inflammable air, and much of the air disappear, the metal is not revived. But not only may the calces of metals imbibe much phlogiston before their complete revival in a metallic form, but other substances also appear to do the same. After heating calcined alum in inflammable air, it became black, and the air was diminished one-fifth. The inside of the vessel in which the process was made had also a black coating. And brick, which contains iron ore, becomes black in the same circumstances; but it is not even attracted by a magnet afterwards. Pounded flint glass becomes black, and absorbs inflammable air, when it is melted in it with a burning lens; but no lead is formed.
- 8. I have observed that when a mixture of dephlogisticated and inflammable air is exploded, acid is produced if there be any excess of the dephlogisticated air, but only water with phlogisticated air if there be any excess of the inflammable air. These proportions I endeavoured to ascertain, and I found that acid is formed when 100 measures of inflammable air are united to 51 measures of dephlogisticated air; but that only water was produced when 100 measures of inflammable air were united to 47 measures of dephlogisticated air.